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13. ABSTRACT (Maximum 200 words) The present study indicates that optimization of microstructure can improve the microwave conductivity of $YBa_2Cu_3O_{7-x}$ . Optimum microstructure here refers to large grain size and better grain-to-grain contact. (2) In the present study we determined that $YBa_2Cu_3O_{7-x}$ processed (oxygen annealed) at 960°C and 975°C yield grain size in the range of 60µm - 150µm. (3) Addition of the optimum amount of gold to $YBa_2Cu_3O_{7-x}$ results in a sharp superconducting transition and zero resistivity temperatures. (4) Addition of gold also improves the microwave conductivity of $YBa_2Cu_3O_{7-x}$ . (5) $YBa_2Cu_3O_{7-x}$ processed at 960°C has conductivity equal to about 90% the conductivity of copper at 16 GHz. Addition of 10% of gold to this material increases its conductivity to about 97% of the conductivity of copper at about 16 GHz. Addition of 20% of gold to this material deteriorates its microwave conductivity. (6) Interpolation of the results on microwave conductivity at 16 GHz to lower frequencies suggests that at lower frequencies our material has microwave conductivity higher than that of copper.			
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FABRICATION OF MICROWAVE WAVE GUIDES  
USING  
HIGH  $T_c$  SUPERCONDUCTORS

AMT  
APOSR-TR- 90-0510

FINAL REPORT

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## 1.0. INTRODUCTION

The objective of this study was to produce bulk high  $T_c$  superconductor  $YBa_2Cu_3O_{7-x}$  with microwave conductivity at least as good or better than that of copper. The subsequent aim was to fabricate cylindrical wave guide using this material. The ultimate goal of this study is to produce  $YBa_2Cu_3O_{7-x}$  with microwave conductivity exceedingly higher (at least two orders of magnitude better) than that of copper. In principle, this is possible if the microstructure of the superconductor material is carefully controlled.

The above-stated goal could be easily achieved if the large single crystals of  $YBa_2Cu_3O_{7-x}$  are available or if the inside surface of a suitable substrate material in the form of hollow cylinder, could be coated with the superconductor material of high quality. The former approach, currently, seems to be far from practical realization. A great deal of work on producing high quality epitaxial films of  $YBa_2Cu_3O_{7-x}$  has been and is being carried out at a number of academic and industrial institutions. However, to the best of our knowledge, practical utilization of thin film high  $T_c$  superconductors to fabricate microwave wave guide has not been achieved so far. Therefore, in the present work the alternative to produce bulk  $YBa_2Cu_3O_{7-x}$  with microwave characteristics comparable to or better than that of copper was selected. At microwave frequencies, the electromagnetic waves do not penetrate in a conductor to a great extent (due to skin effect), and conduction takes place mainly at the surface. Hence, the integrity of the superconductor surface is of great importance. At present all the thin films and bulk superconductor materials are produced in a poly crystalline form only. Therefore, the grain to grain interconnect over the surface is very essential. In order to achieve this goal, the work was focused at the following specific points:

1. Optimization of the process parameters to obtain reproducible  $YBa_2Cu_3O_{7-x}$  with  $T_c > 90^\circ K$ .
2. To obtain  $YBa_2Cu_3O_{7-x}$  with largest possible grains with better grain to grain interconnect.
3. To study the effect of the addition of gold to improve the grain to grain interconnect.

It was found during the present study that for the fixed time, the oxygen annealing temperature was the limiting factor for the grain size. Also, addition of the optimum amount of gold to  $YBa_2Cu_3O_{7-x}$  not only improved the  $T_c$  of the material, but also increases the grain size. To the best of the authors' knowledge, this favorable effect of gold has not been reported in the U.S. open literature and is reported here for the first

time. Detailed study of the effect of the addition of gold to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  needs further research. The microwave conductivity measurements were carried out at the COMSAT laboratories with the help of Dr. Andrew Meulenberg. Microwave conductivity was determined by measuring the quality factor,  $Q$ , of a reflecting resonance cavity operating in  $\text{TE}_{011}$  mode. At about 16 GHz and 77°K conductivity of gold mixed  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was found to be about the same as that of copper. For  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor material, the conductivity varies as the inverse of square of the frequency. This means at 8 GHz this superconductor material has conductivity about 4 times better than that of copper.

## 2.0 EXPERIMENTAL

2.1 Synthesis of high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ : During the present study the samples were synthesized from high purity  $\text{Y}_2\text{O}_3$  (99-999%),  $\text{BaCO}_3$  (99-997%), and  $\text{CuO}$  (99-999%) supplied by AESAR (Johnson Matthey). The stoichiometric mixture of these three oxides was ground and mixed in agate mortar and pestle. Thin pellets were formed from this mixture using stainless steel dies and hydraulic press. Pellets of two diameters, i.e. 0.75" and 0.50" in the thickness range of 2.5mm to 8mm were made during this study. These pellets were calcinated at 950°C in a  $\text{O}_2$  environment using a computer controlled furnace for about 18 hours. The reacted material samples were then removed from the furnace and then ground in mortar and pestle. Using this powder, the pellets were formed by compression. In case the initial pellets were thicker than 4mm, the material was once again reacted under the same condition to ensure the proper composition and stoichiometry of the resulting material. The stoichiometry of the powder/pellets was also checked by x-ray diffraction. Once the formation of the stoichiometric material was ensured, the next step was the oxygen annealing of samples in the pellet forms. The pellets were made from presynthesized  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by compression in a pressure range 3.5kbar to 9.5kbar. During the oxygen annealing material was cooled to room temperature at the rate of 2°C/min. To study the effect of the addition of gold during the present work,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples containing 10% by weight and 20% by weight of gold were prepared. High  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder and required amount of 99.95% pure gold flakes (1-3µm particle size) were mixed in a dry bottle. The mixture of these powders was then used for making pellets by compression and were subsequently oxygen annealed. For making cylinders of high  $T_c$   $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , a special stainless steel die set was made. This die set can make cylinders with length up to 1 inch and outer and inner diameters of 0.75 inch and 0.50 inch, respectively.

2.2 X-ray diffraction using a curved position sensitive detector: To identify and ascertain the superconducting phase in the specimen prepared by the above-mentioned method, x-ray diffraction method was used. The experimental system in the present work consisted of the following major components:

1. GE XRD-7 x-ray generator with CA8-F/Cu x-ray tube,
2. Spectrogoniometer,
3. Silicon crystal monochromator,
4. Sample holder, and
5. Curved Position Sensitive Detector (CPSD) with data acquisition analysis and storage accessories.

The schematic of the experimental system is shown in Figure 1. As opposed to the conventional diffractometric system, the CPSD used for this work is a novel x-ray detector. It has an angular range of  $120^\circ$  and diffraction peaks/lines in this range can be simultaneously obtained without moving the detector. A special holder to mount the CPSD on the spectrometer was fabricated. A detailed description of the CPSD and the calibration procedure is given in Appendix A.

2.3 D.C. resistivity measurements: Resistivity measurements were done using four probe techniques. Contacts were made using thin copper wires and silver paint. Keithley 197 autoranging microvoltmeter, Keithley 224 programmable constant current source, and Keithley 740 system scanning thermometer were used along with IBM PC for these measurements. The sample was cooled to liquid nitrogen temperature and was allowed to warm-up in a natural fashion. A constant current of 1mA and 10mA were applied, and the voltage was measured using a microvoltmeter at various temperatures. The data collected by the personal computer were graphically plotted as relative resistivity versus temperature.

2.4 Microwave conductivity: Microwave conductivity of the superconducting samples have been determined at COMSAT Laboratories with the help of Dr. Meulenberg. The measurements on superconductor as well as copper samples of the same dimensions were made at liquid nitrogen temperature. Microwave conductivity was determined by measuring the quality factor,  $Q$ , of a reflecting resonance cavity operating in  $TE_{011}$  mode. Results for a cavity having an endplate replaced with the sample were referenced against those for a cavity with an absorbing endplate. The  $Q$  of a cavity is determined [1,2] by measuring the loss in reflected power at resonance, calculating the level at half maximum (or some other fixed percentage level), and interpolating between data points to determine the frequencies corresponding to this level. The value obtained from the center frequency ( $f_c$ ) divided by the frequency difference between the half-maximum points ( $\Delta f$ ) is the loaded  $Q$  ( $Q_L$ ) of the system.

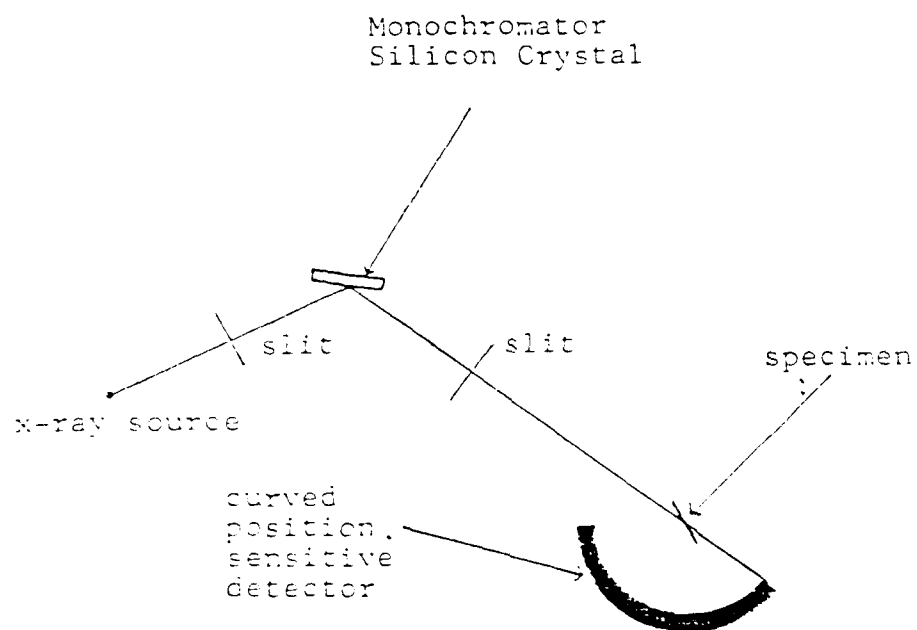


Figure 1. Schematic illustrating the experimental diffraction system.

2.5 Optical microscopy: The microstructure of the samples was studied using an Olympus inverted metallurgical microscope (Model PME). Samples were observed with both the normal and polarized light. A superconductor phase can be normally identified by the presence of twins in the grain when viewed using polarized light. The photographs revealing the microstructure of samples were taken using polaroid type 55 films.

### 3.0 RESULTS AND DISCUSSION

The synthesis of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  involve two major steps.

1. Calcination of the starting ingredients (i.e.  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ ) to obtain the stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .
2. Oxygen annealing of the stoichiometric phase where slow cooling of the sample from the annealing temperature is very essential to obtain superconducting phase.

These steps involve the following material/process parameters.

1. The purity of starting ingredients.
2. Pressure used for the compression of pallets.
3. Particle size distribution in the material to be compressed.
4. Calcination and oxygen annealing temperatures.
5. Calcination and oxygen annealing time.  
and
6. The rate of cooling (after oxygen annealing).

During the entire course of the reported study the highest purity materials available were used. The oxygen annealing was carried out at 650-700 Torr. This oxygen pressure range was determined to be optimum. The calcination temperature used during this study was  $950^\circ\text{C}$  and was kept constant during the entire study.

When pallets of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powder were made for oxygen annealing, the particle size distribution in the powder did not seem to have any effect on the transition temperature. However, the powder containing smaller particles required higher pressure for the pallet compression. The void density and void size in the pallets made from smaller particles were less as compared to those in pallets made from larger particles. These effects are illustrated in Figures 2(a) and 2(b). The photograph in Figure 2(a) shows the microstructure of the surface of the pallet made from the powder having



particle size in the range of 44 $\mu$ m - 74 $\mu$ m. The sample shown in Figure 2(b) contained particles in the size range of 74 $\mu$ m - 149 $\mu$ m. Figures 3(a) and 3(b) show the four probe D.C. resistivity measurements on the pallets in Figure 2(a) and 2(b), respectively. Both samples show  $T_c$  onset of 95°K with zero resistivity at 90°K. The data scatter in these initial measurements is due to using a low applied current (1mA) and, therefore, the digital microvoltmeter at the lower limit of resolution.

The effect of the pressure (during compression of the pallets) was studied during in the initial period of this work. Pressures in the range 3.5kbar to 9.5kbar were used. In this range the pressure did not have significant effect on the transition temperature. However, the packing density of the compacted material changed significantly. For 5mm thick pallet the packing density varied from about 48% at 3.5kbar to about 81% at 9.5kbar. Figures 4(a), 4(b) and 5(a), 5(b) illustrates the effect of pressure on the microstructure. Figure 4(a) is a microphotograph of a surface of the pallet compressed at 3.5kbar. Figure 4(b) is the microphotograph of the surface of the same pallet after oxygen annealing at 960°C. Figure 5(a) and 5(b) are the microphotographs of the pallet compressed at 9.5kbar surface before and after the oxygen annealing at 960°C. For both samples, the particle size distribution of the starting  $YBa_2Cu_3O_{7-x}$  powder was the same. After compression, the pallet compressed at higher pressure (9.5kbar) has relatively much smaller particle/grain sizes. After oxygen annealing, both samples have the same average grain size. However in a sample which was compressed at 9.5kbar, the grain to grain interconnect is much better and the density of voids and "unfaceted" phase is lower than that in the pallet compressed at 3.5kbar. Figure 6(a) and 6(b) show results of the D.C. resistivity measurements of these samples. These results indicate that they have the same transition temperatures. At this time, we do not know if the "unfaceted" phase in the sample surface mentioned earlier is also superconducting. It is required to further study this unfaceted phase using electron microscopy and electron microprobe analysis techniques. The packing density and, hence, the pressure will be of critical importance when it is required to transmit a very high current density through the bulk of a sample.

(X800)

(a)



(b)



Figure 2 Microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pellets prepared using the powder with particles in the size range (a) 44 - 74um and (b) 74 - 149um, respectively.

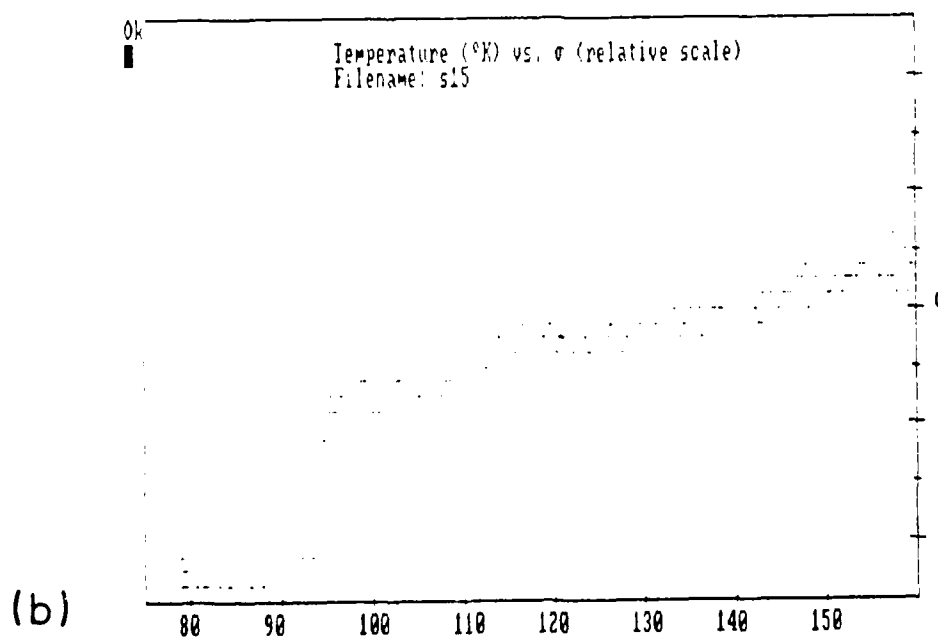
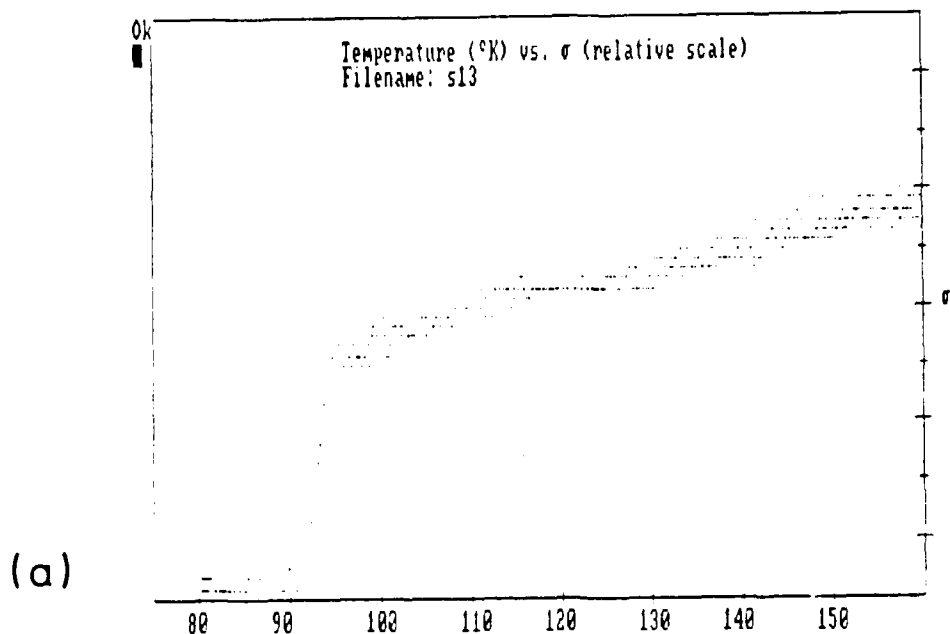
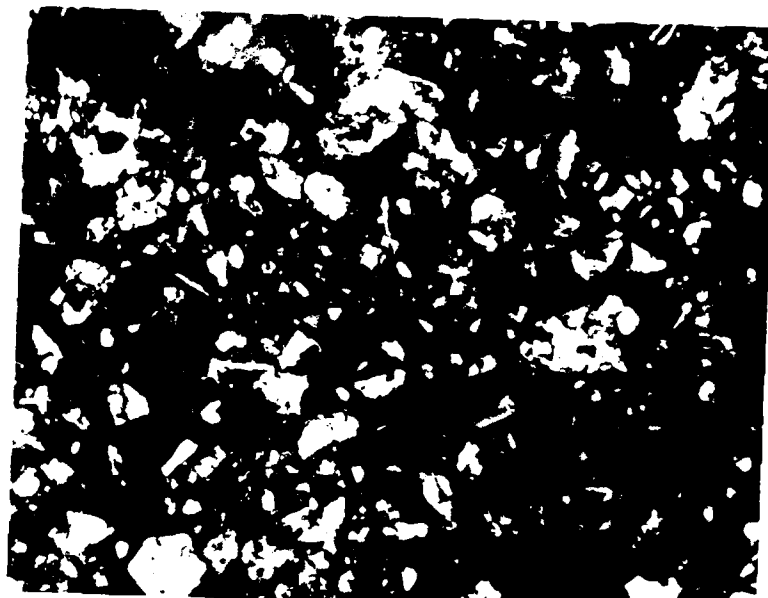


Figure 3 D.C. resistivity measurements on the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  prepared using the powder with particle size distribution in the range (a) 44 - 74 $\mu\text{m}$  and (b) 74 - 149 $\mu\text{m}$ .

(X800)

(a)



(b)

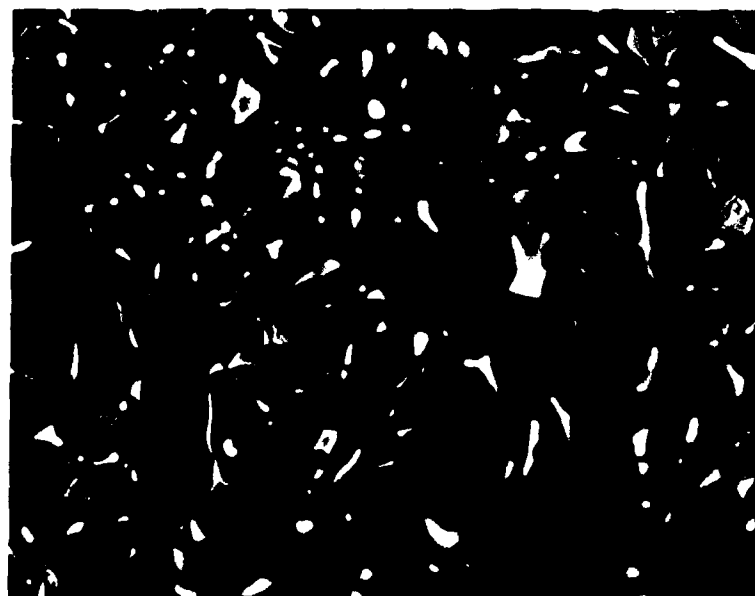
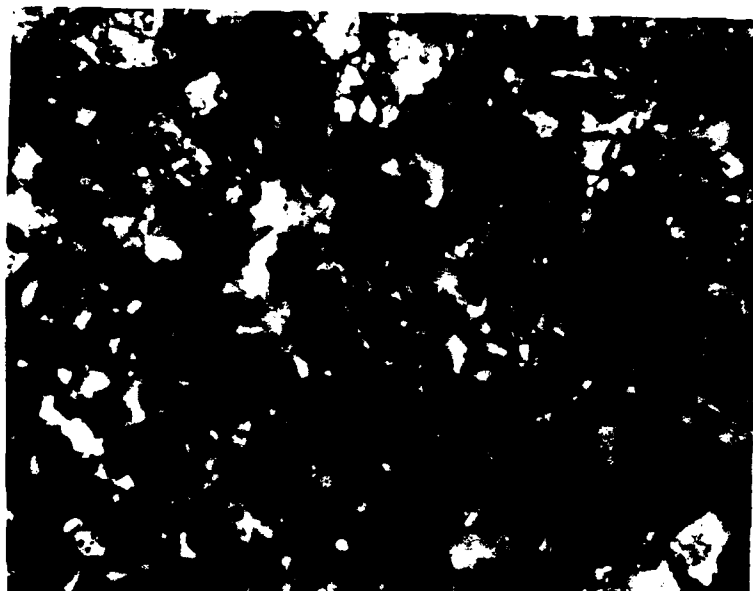


Figure 4 Micro-photograph showing the microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pallet compacted using the pressure of 3.5kbar (a) before (b) after oxygen annealing.

(X800)

(a)

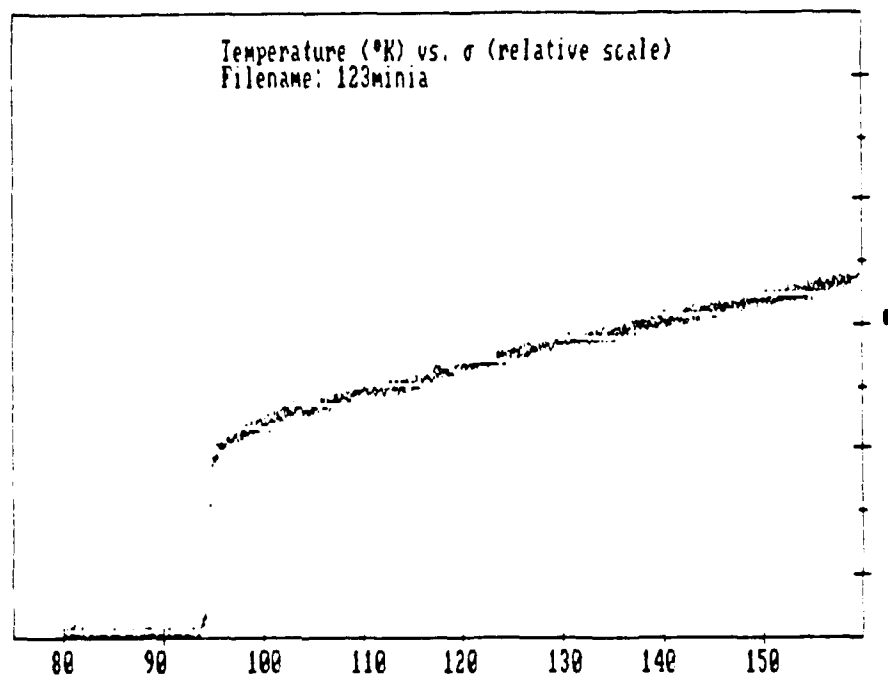


(b)



Figure 5 Photograph showing the microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pallet compacted using the pressure of 9.5kbar (a) before and (b) after oxygen annealing.

(a)



(b)

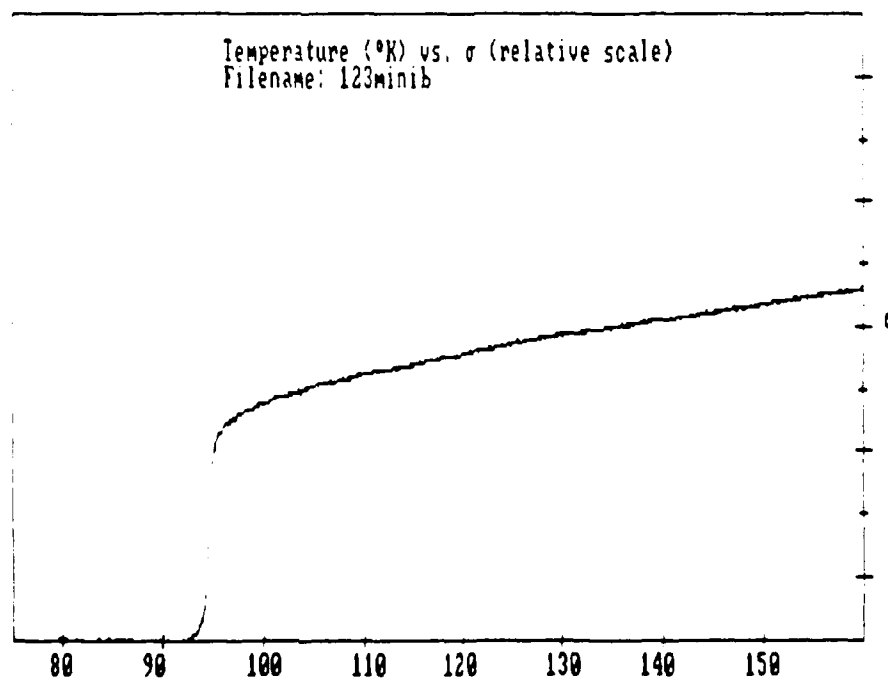


Figure 6 D.C. resistivity measurements on  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  pallets prepared using (a) 3.5 kbar and (b) 9.5 kbar pressure, respectively.

The effect of temperature on the microstructure during oxygen annealing was studied at three different temperatures of 945°C, 960°C, and 975°C. Above 975°C  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is believed to decompose and phase separation takes place resulting into Ba and Cu poor material [3]. As expected in sintering process the grain size was found to increase with increasing temperature. Figures 7(a), 7(b), and 7(c) show the microstructure of the samples oxygen annealed at 945°C (sample A), 960°C (sample B), and 975°C (sample C). In Figure 7(a) a fine network of small faceted grains (1-6µm) separated by unfaceted regions and voids can be seen. Compared to Figure 7(a) in Figure 7(b) a significant increase in grain size is obvious. Grains as large as 50-60µm were observed. At the same time the size of unfaceted phase and voids also increased in size as compared to those in specimen in Figure 7(a). In Figure 7(c), which is a microphotograph of a surface of the specimen annealed at 975°C, the largest grain size among the specimen studied here is observed. Most of the grains in this sample are separated by the unfaceted phase or voids. The composition of the three samples discussed above was checked using x-ray diffraction. X-ray diffraction patterns of these sample area shown in Figures 8(a), 8(b), and 8(c) are in good general agreement with earlier reported [4] patterns for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The D.C. resistivity data of these samples are presented in Figure 9(a), 9(b), and 9(c) which shows the superconducting transition temperature onset at about 96°K, 94°K, and 93.8°K respectively. However, the zero resistivity is observed at about 93.8°K in Figure 9(a) and at about 92.5°K for samples with data in Figure 9(b) and 9(c), respectively. The transition width is minimum for the samples containing largest grains (i.e. Figure 9(c)). The microwave measurement data on these samples are shown in Table I.

As mentioned earlier microwave measurements involved measurement of quality factor  $Q$  of a reflecting resonance cavity in  $\text{TE}_{011}$  mode. The  $Q$  of cavity is easy to measure and can be determined using the relation:  $Q = \text{center frequency} / 3\text{db bandwidth}$ . In the present case  $Q$  for the cavity having an endplate replaced with the superconductor sample were referenced against those for a cavity with a copper end plate. In this configuration the surface resistance of a superconductor sample can be determined using the following expression:  $R_s = \text{geometric factor} \times (1/Q_{\text{Cu}} - 1/Q_s)$  where  $Q_{\text{Cu}}$  is the quality factor of the cavity with copper as endplate and  $Q_s$  is the qualifactor of the cavity wish superconductor sample as an endplate.

Now let us consider the results in Table I. At liquid nitrogen temperature the material with the largest grain size has  $Q/Q_{Cu} = 0.91$ . To first approximation we can say that conductivity of this sample at 77°K and about 16 GHz is 91%

TABLE I

SAMPLE	TEMP	$C_f$ (GHz)	$\Delta_f$ (MHz)	$Q = C_f/\Delta_f$ (x1000)	n	$Q_s/Q_{Cu}$
copper	RT	15.434	1.2	12.86	0.5	--
copper	LN <sub>2</sub>	15.491	0.6	25.82	0.5	--
A	RT	15.644	3.8	4.12	2.5	0.32
A	LN <sub>2</sub>	15.701	0.8	19.63	.55	0.76
B	RT	15.220	2.8	5.43	1	42.2
B	LN <sub>2</sub>	15.270	0.7	21.8	2	0.84
C	RT	15.223	2.6	5.85	2.8	0.45
C	LN <sub>2</sub>	15.269	0.65	23.49	0.8	0.91

$C_f$  - Center Frequency

$\Delta_f$  - Frequency Bandwidth

n - Coupling Coefficient

$Q_s/Q_{Cu}$  - Ratio of the quality factor of cavity with superconductor as endplate to quality factor of the cavity with copper as endplate. This ratio for each sample is calculated at room temperature and liquid nitrogen temperature.

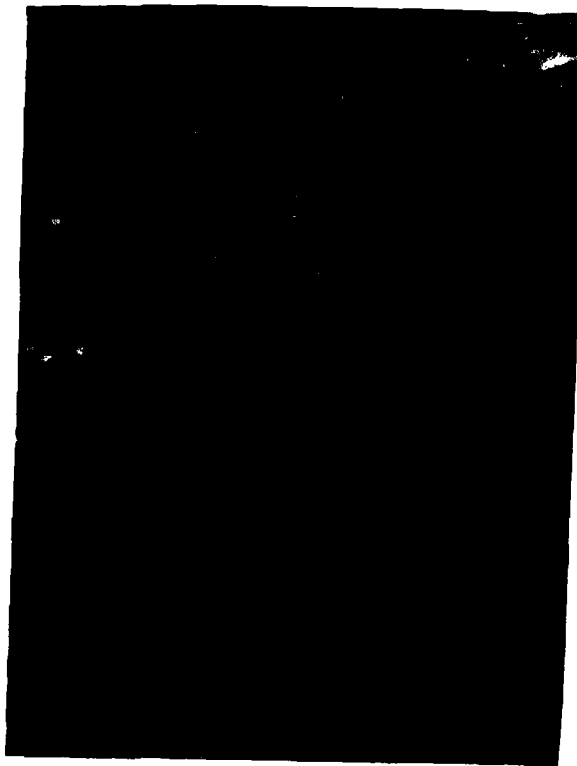
RT - Room Temperature (about 300°K)

LN<sub>2</sub> - Liquid Nitrogen Temperature (77°K)

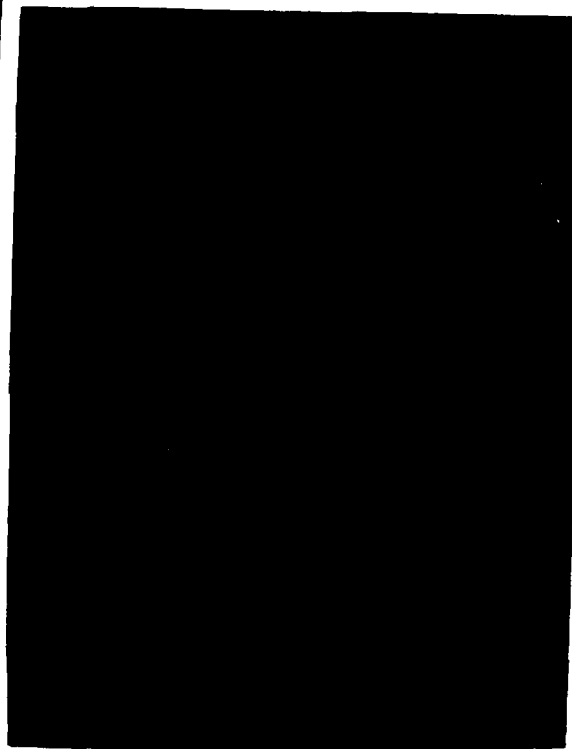




(a)



(b)



(c)

(X800)

Figure 7 Photographs showing the microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples processed at (a)  $945^\circ\text{C}$  (sample A), (b)  $960^\circ\text{C}$  (sample B), and (c)  $975^\circ\text{C}$  (sample C), respectively. Increase in grain size with increasing processing temperature can be easily observed in these photographs.



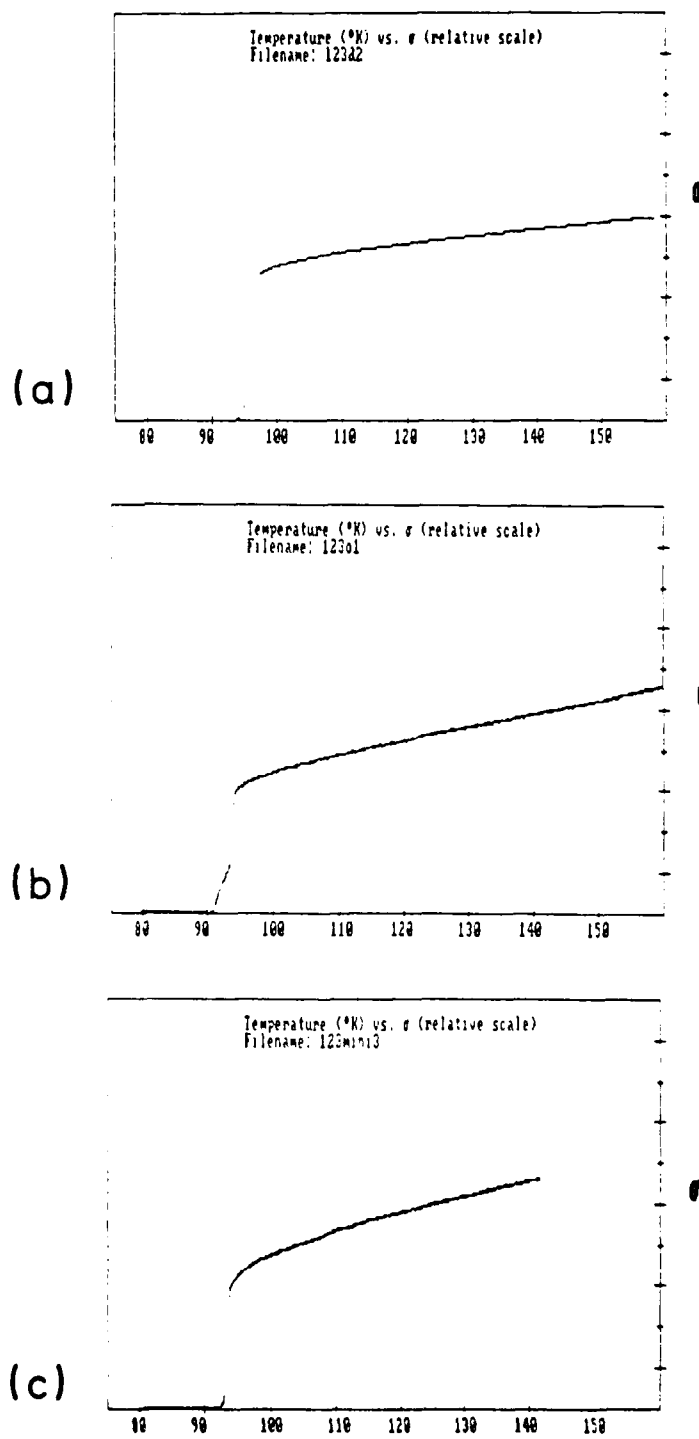


Figure 9 Results of D.C. resistivity measurements on (a) sample A, (b) sample B, and (c) sample C, respectively.

the conductivity of copper. The conductivity of copper changes as  $1/f^{1/2}$  and that of superconductor changes as  $1/f^2$ . Therefore, at lower frequencies in microwave range conductivity of these  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples will be significantly larger as compared to copper. In comparison to copper the superconductor samples do have at least metallic conductivity at room temperature and it increases with grain size and improved grain to grain interconnect.

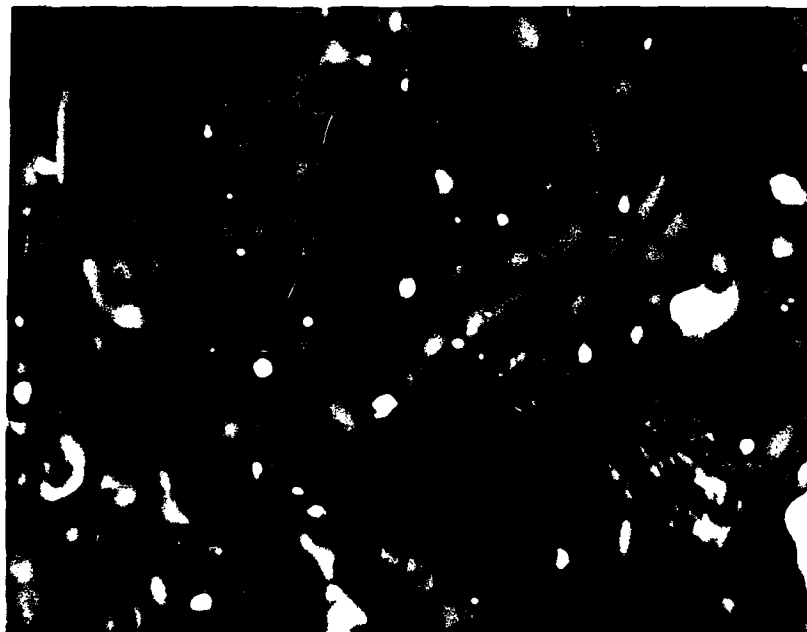
In the present measurements copper samples with the same dimension as superconductor samples were prepared. The shape of the samples were identical (i.e. cylindrical pellets) and the external dimensions were the same within 10%. However, the copper samples were in the form of solid slugs whereas superconductor samples were in the form of compacted and sintered discs with the packing density in the range of 60% to 80%. Hence, even in the best case sintered material does not have the surface as continuous as the casted material. Also, the grains in sintered material are not all oriented in a same crystallographic direction. It has been suggested [4] that in low temperature superconductors superconducting islands are connected by resistive paths. Similar resistive paths can be expected in high temperature superconductors if the microscopically observed intragranular "unfaceted" regions are not superconducting at 77 K. Meulenberg et al. [1] had suggested a material model for high  $T_c$  superconductors. According to this model bulk high  $T_c$  superconductor materials involve superconducting paths that are nonlinear and particularly just below the critical temperature may be circuitous. For DC measurements, such meandering paths have only a small effect which is seen during the onset of superconducting behavior. At this stage, intense magnetic fields from high local current densities can quench the superconductivity and force the current to flow, for short distances, through alternative paths, which may include resistive material. At high frequencies circuitous paths which result in self and mutual inductance can generate back-emfs that oppose current flow along the path and thus divert current through resistive channels. These inductive effects will increase with frequency. As temperatures are lowered below  $T_c$  and more superconducting paths are opened up, the current flows become more linear and the self inductance is reduced. Most applications require high conductivity and not zero resistance. Therefore, a means of reducing the inductive element of HTS materials, even at the expense of slightly increased resistive components, would be highly desirable. This could be accomplished by filling the voids in bulk HTS materials with high-conductivity materials. In the present case we used gold to fill these voids and test this model. At present we do not understand the nature of intragranular unfaceted material which is encountered the most in the material processed at 975°C. Hence, we decided to add gold in material processed at 960°C,

which has at least 50-60  $\mu\text{m}$  sized grain and has less of unfaceted material present in intergranular space. Using the same base material as in sample "B" we prepared HTS sample containing 10% gold by weight. The specimen weight and size were kept same as sample "B" and this sample was processed under identical conditions as the sample "B." We labeled this gold doped sample as "BG." Figure 10 is a microphotograph showing the grain structure of a sample "BG." The bright white spots in the photograph are gold particles. Comparing the microstructure of sample BG with that of Sample B (Figure 7(b)) it can be seen that the average grain size in gold doped sample is larger than that in the undoped sample. Authors have not come across a report in open literature, indicating the effect of gold doping to increase the grain size in these materials. Other effect of addition of a gold to this was found on the transition temperature. Figure 11 shows the results of D. C. resistivity measurements on gold doped sample. Addition of gold not only makes the superconducting transition sharp, but also increases the transition temperature by a few degrees. This can easily be seen by comparing Figure 9(b) with Figure 11. Superconducting grains in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  can be identified by the presence of twins when observed under polarized light. A number of pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and 10% gold doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  were observed under polarized light. In general most of the grains in gold doped samples showed the presence of twinned structure opposed to grains in undoped samples. Typical microstructure of gold doped and pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples observed using polarized light is shown in Figure 12(a) and 12(b).

The sample "BG" had a rough wedges around the periphery of the sample and reliable microwave measurements could not be carried out on this sample due to mounting problems. Hence, a new set of samples for the systematic study of the effect of gold were prepared.

About 50 gm of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was synthesized in pallet form at the processing temperature of  $960^\circ\text{C}$ . Out of this material three pallets each weighing about 2.5 gm and having diameters of 0.75 inch were made. The first pallet (sample X) was made of pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The second (sample Y) was doped with 10% gold (by weight), and the third pallet (sample Z) was doped with 20% gold.

The microstructure of these three superconducting pallets (i.e. X, Y, and Z) are shown in Figures 13(a), 13(b), and 13(c) respectively. The sample X consists of many faceted grains, most of which are columnar. The effect of addition of gold can be seen in the microstructure of sample Y. Sample Z, which contains 20% of gold by weight, also shows some grain growth, but is not as prominent as seen in sample Y. Sample Z also contains the large regions filled with



(X800)

Figure 10 Photograph showing the effect of the addition of gold on the microstructure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . This sample was made using base material as in sample B and adding 10% gold by weight to it. It can be seen that compared to grain in sample B (Figure 7b) this sample has larger grains.

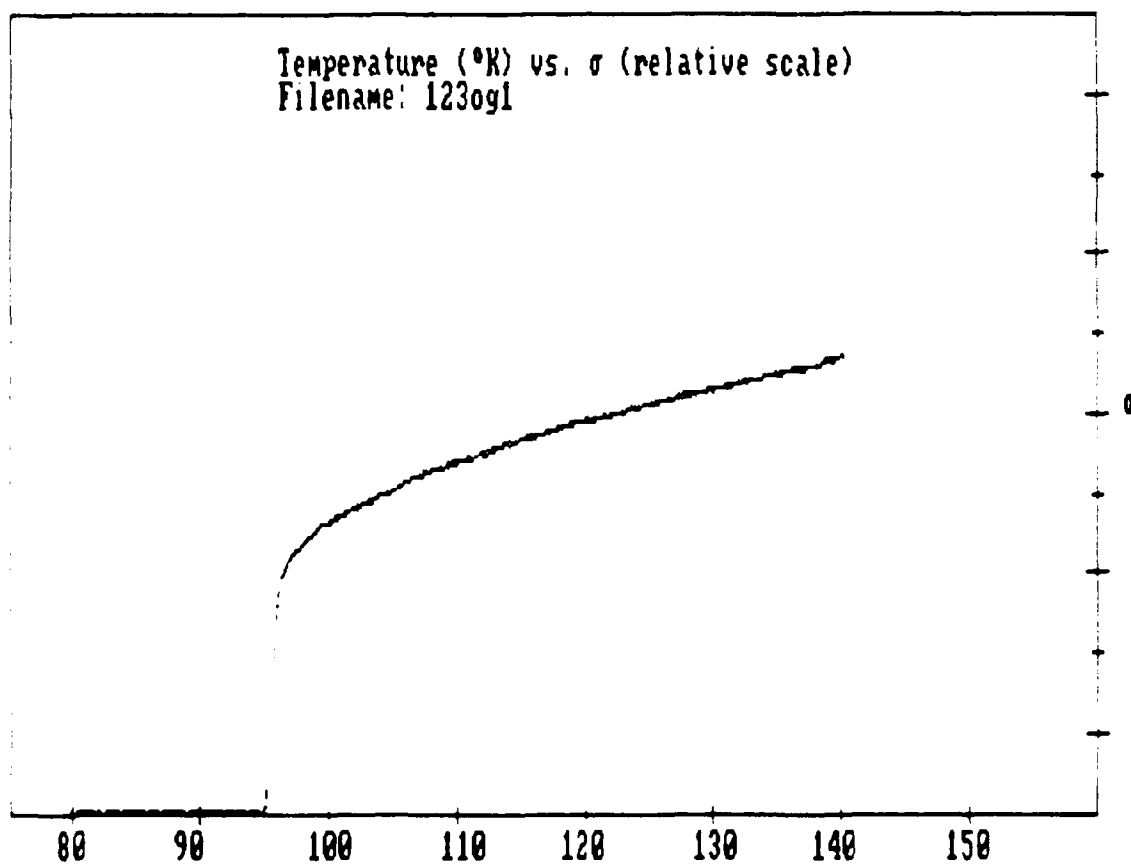


Figure 11 Results of D.C. resistivity measurements on gold doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample (sample BG).

(X500)

(a)



(b)



Figure 12 Microstructure of (a) pure and (b) gold doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  samples observed using polarized light. The grains with twinned regions indicate the presence of superconducting phase.





(a)



(b)



(c)

Figure 13 Photographs showing microstructures of pure and gold doped samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . (a) pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (sample X), (b)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  containing 10% gold by weight (sample Y), and (c)  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  containing 20% gold by weight (sample Z). (X400)

gold. These three samples were first characterized with respect to D.C. resistivity (Figures 14[a,b,c]). Then the microwave measurements were carried out on these samples (Table II). Finally, the A.C. susceptibility measurements were carried out on these samples (Figures 15[a,b,c]). The A.C. susceptibility measurements were carried out on pieces of about 5mm x 2mm x 2mm size. Both D.C. resistivity and A.C. susceptibility results suggest that superconducting properties can be enhanced by the addition of optimum amounts of gold. In order to determine this optimum amount, a further transient study with gold doping in the range of 0-20% gold is needed, which will be a subject of future study. Results of microwave measurements presented in Table II show that  $Q$  of the superconductor material containing 10% gold (sample Y) is almost equal to that of copper at 16 GHz. Understanding of exact mechanism by which gold in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  increases the grain size and improves the D.C. as well as microwave conductivity needs the detailed investigation.

TABLE II

SAMPLE	TEMP	$C_f$ (GHz)	$\Delta_f$ (MHz)	$Q = C_f/\Delta_f$ (x1000)	n	$Q/Q_{Cu}$
copper	RT	15.707	1.1	14.28	6.3	--
copper	77°K	15.759	0.6	26.26	4.2	--
X	RT	15.312	2.5	6.12	4.2	.43
X	77°K	15.361	0.65	23.63	.75	.90
Y	RT	15.295	2.8	5.46	3.2	.38
Y	LN	15.342	0.60	25.57	0.66	.97
Z	RT	15.219	2.6	5.85	1	.41
Z	LN	15.335	0.7	21.91	.8	.83

The improvement in electrical conductivity may be explained, qualitatively, in terms of improved grain-to-grain contact. Also, gold will prevent the loss of oxygen from superconductor material at the sites where gold particles are localized. Grain growth similar to we have reported here was observed by Jeffrey and Archer [6] in case of sintered tungsten. The presence of thorium oxide, which is insoluble in tungsten, was found to have increased the grain growth in sintered tungsten when added in optimum concentration. When the amount of thorium oxide exceeds the optimum level, it impedes the formation of large grains.

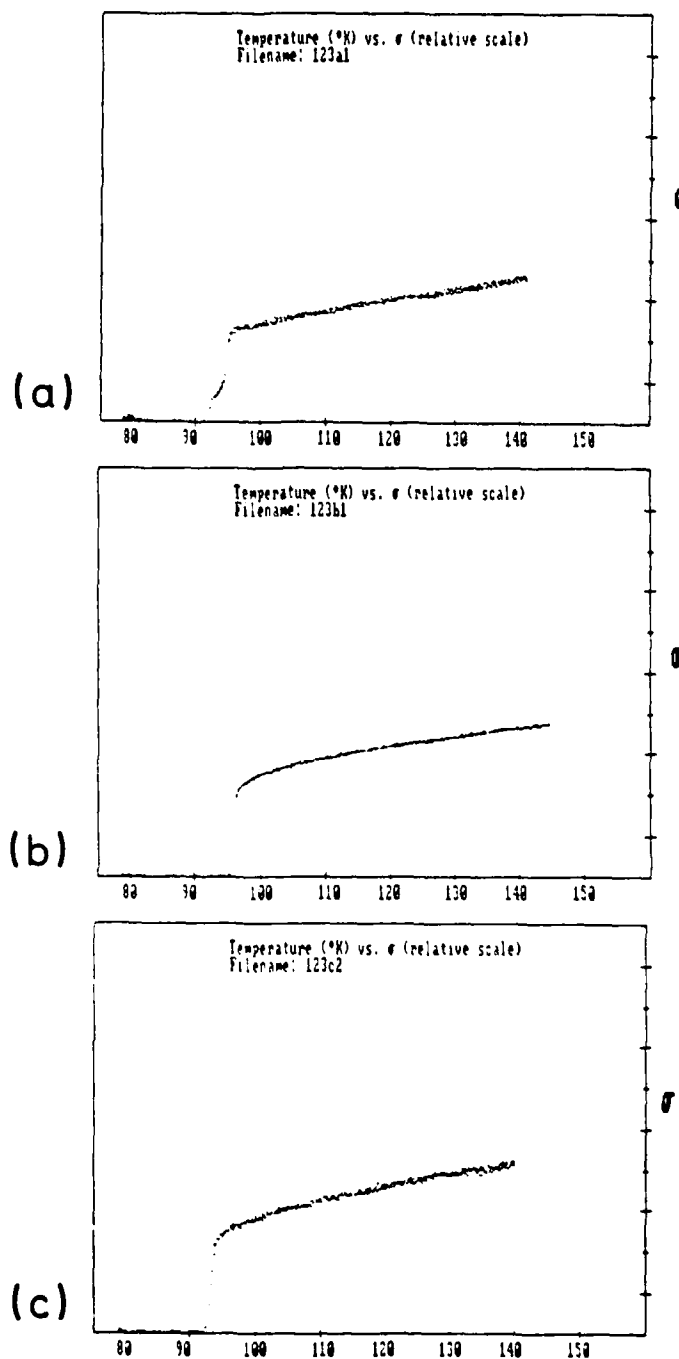
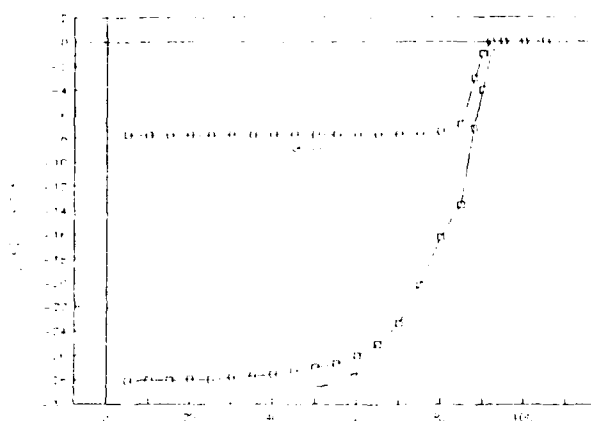


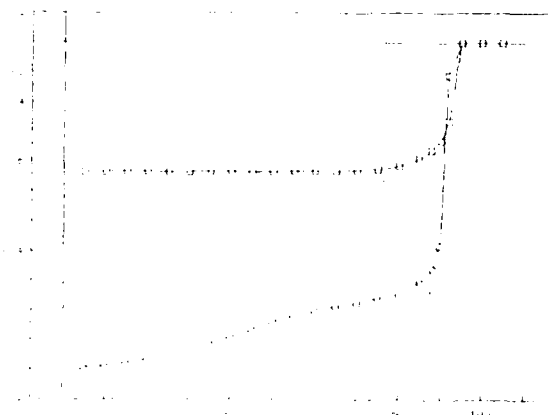
Figure 14 Results of D.C. resistivity measurements on (a) sample X, (b) sample Y, and (c) sample Z. It can be seen in (b) that with addition of 10% gold (by weight) to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  the superconducting transition becomes sharp and the  $T_c$  and zero resistance temperature increases. As seen in (c) with increasing gold content, the superconducting properties deteriorates.

(a)



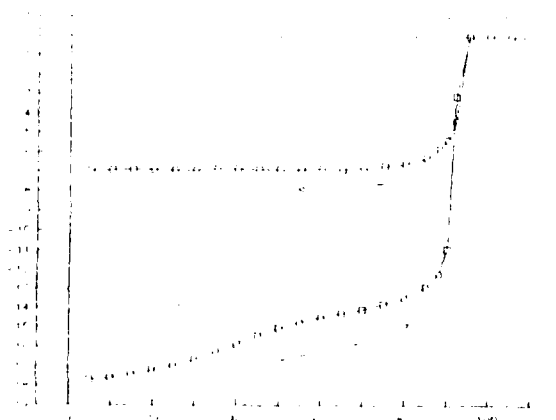
1123 sample X : F  
100°C

(b)



EE sample Y : F  
100°C

(c)



EE sample Z : F  
100°C

Figure 15 Results of A.C. susceptibility measurements on (a) sample X, (b) sample Y, and (c) sample Z. These results are in agreement with D.C. resistivity measurements shown in Figure 14a,b,c.

Using the material from the same batch which was used to make samples X, Y, and Z, two cylinders of length 0.5", inner diameter 0.5" and outer diameter 0.75", were fabricated. One cylinder was made of pure  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and the second was doped with 10% (by weight) of gold. These cylinders were processed (oxygen annealed) at 960°C and found to have the same microstructure as pallets X and Y respectively. The x-ray diffraction pattern of these cylinders showed the presence of major peaks of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . These patterns are presented in Figure 16. These two cylinders will be delivered along with this technical report. Two more similar cylinders were made using the pure and 10% gold doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Attempts to measure the Q factor (at microwave frequencies) of cavities made using these cylinders are in progress. These measurements will also be carried out at COMSAT laboratories.

The present study does indicate the microwave properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  can be improved by optimizing its microstructure. There are two more ways in which the grain size and grain-to-grain contact can be improved. The first method is lowering the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample through a steep gradient. Initially, this method was used by R.C. DeVries [7] for the growth of large grains of barium titanate. Later, this technique has been applied to other materials by various workers.

The second method is a quench and melt growth process suggested by Masato Murakami [8]. The feasibility of this technique to obtain  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  of superior structure has been demonstrated by Japanese researchers. However, this process still requires optimization of several process parameters.

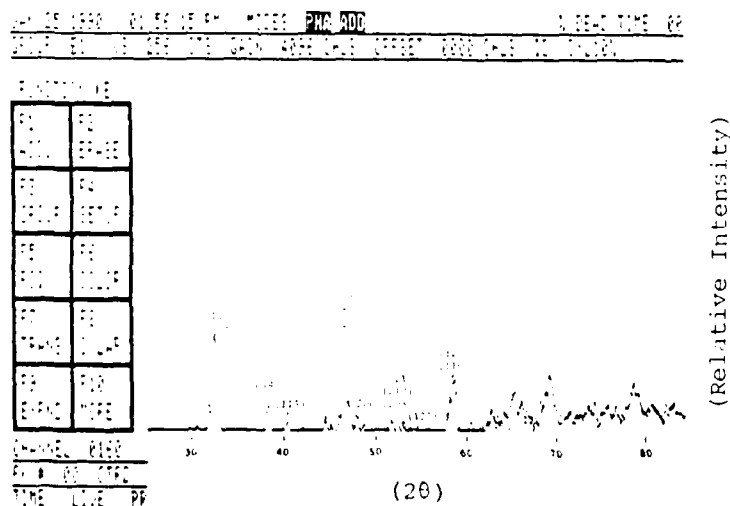


Figure 16 X-ray diffraction pattern of (a) pure and (b) gold doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  cylinders.

#### 4.0 CONCLUSION

1. The present study indicates that optimization of microstructure can improve the microwave conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Optimum microstructure here refers to large grain size and better grain-to-grain contact.
2. In the present study we determined that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  processed (oxygen annealed) at  $960^\circ\text{C}$  and  $975^\circ\text{C}$  yield grain size in the range of  $60\mu\text{m} - 150\mu\text{m}$ .
3. Addition of the optimum amount of gold to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  results in a sharp superconducting transition and also increases the superconductor transition and zero resistivity temperatures.
4. Addition of gold also improves the microwave conductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .
5.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  processed at  $960^\circ\text{C}$  has conductivity equal to about 90% the conductivity of copper at 16 GHz. Addition of 10% of gold to this material increases its conductivity to about 97% the conductivity of copper at about 16 GHz. Addition of 20% of gold to this material deteriorates its microwave conductivity.
6. Interpolation of the results on microwave conductivity at 16 GHz to lower frequencies suggests that at lower frequencies our material has microwave conductivity higher than that of copper.

#### 5.0 ACKNOWLEDGMENTS

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## Appendix A

### Description of CPSD and its calibration.

In x-ray diffractometry experiments, observations with a good spatial resolution over a wide range are required. CPS 120 can be mounted on all kinds of goniometers now available on the market and its electronic data can be processed by all data processing systems. CPS 120 is a sophisticated tool which uses the latest developments in detector technology. CPS 120 can replace films and proportional scintillation detectors as well as scanning straight position sensitive detectors with great advantages for all x-ray diffraction applications.

### THE SYSTEM

The CPS 120 system includes:

- The detector with its preamplifier
- The electronic system

The Detector:

The detector is a gas flow blade chamber. It thus has a curved anode accurately located on the circle of the goniometer. The x-ray peak position is obtained through the so-called delay line readout method.

A good spatial resolution - less than  $0.02^\circ$  - is secured with the use of special materials very accurately manufactured. The anode made with a blade can receive the direct x-rays beam.

The anode signal can be used to control the exact count rate of x-rays radiating over the detector. The pulses from both sides of the delay-line serve to calculate the x-ray position impact.

The preamplifier is used to adapt the electronic pulses collected on the delay-line to the electronic system.

The Electronic System:

The electronics is made up of specific NIM modules. Each module has a determined and independent function - the electronic system includes: a PC module (pressure and gas flow control); a HV module (high voltage power supply); a ratemeter module - this is helpful for the tuning of the goniometer and enables to control the count rate of x-rays radiating over the detector.

A APD module - these discriminators accurately define the centroid of pulses coming from the detector and so they help determine the exact position of x-rays. A DDL module is used to add or subtract some delay. This module is useful when the users of CPS 120 want to zoom any part of the x-ray diffraction pattern. A PSP module - it gives the position of x-rays, and its output can be connected to all (analog to digital convertors) available in the market.



CPSD chamber consists mainly of Anode and Cathode, and a stream of ionizing gas (Argon + 15% Ethane) flowing at a constant pressure of 6.5 Bars. A schematic illustrating CPSD construction is shown in Figure 1. When a direct or diffracted beam enters the detector chamber, it ionizes the gas and produces electron-positive ion (cation) pairs.

Due to high voltage between anode and cathode, electrons are attracted to the anode and travel with very high velocity. This produces an electron avalanche. Because the electron avalanche is sharply localized, the point where electrons hit the anode can be electronically determined by measuring the time required for the pulse to travel from the point of impact to the end of the anode. This provides the angular position ( $2\theta$ ) of the x-ray beam. A circuit diagram illustrating operation of CPSD is given in Figure 2. The CPSD used in this work has the angular range of  $120^\circ$ , hence diffraction peaks in this wide range can be simultaneously obtained without moving the detector, unlike the conventional diffractometry.

Before operating the CPSD unit, high purity gas mixture containing Argon and 15% Ethane was allowed to flow at a recommended pressure (6.5 Bars) through the detector chamber for about 24 hours. Using the direct x-ray beam, operation of the CPSD and associated electronics and software has been tested. The height of CPSD was adjusted such that the direct beam is incident in the middle of the chamber. The zero of the detector was adjusted as described in the operation manual. Next, the direct beam was recorded for 60 seconds at various detector positions from one end to the other end. This calibrated channels in terms of angle  $2\theta$  (in degrees). This will help identify peak position for the main as well as diffracted x-ray beams. Table I and corresponding Figure 3 respectively represent the calibration run. Next, this calibration was verified using x-ray diffraction of aluminum. Diffraction pattern for this sample was recorded in  $120^\circ$   $2\theta$  range. The diffraction peaks were identified and matched with JCPDS diffraction file on aluminum. These results are presented in Table II and Figure 4 respectively. Accuracy better than 1% was observed for angles less than  $120^\circ$ . Present CPSD can record  $2\theta$  angles up to about  $150^\circ$ . For angles greater than  $120^\circ$ , the accuracy goes down to 15%. It is recommended for the use in the  $120^\circ$  range with angular resolution of  $0.018^\circ$ .

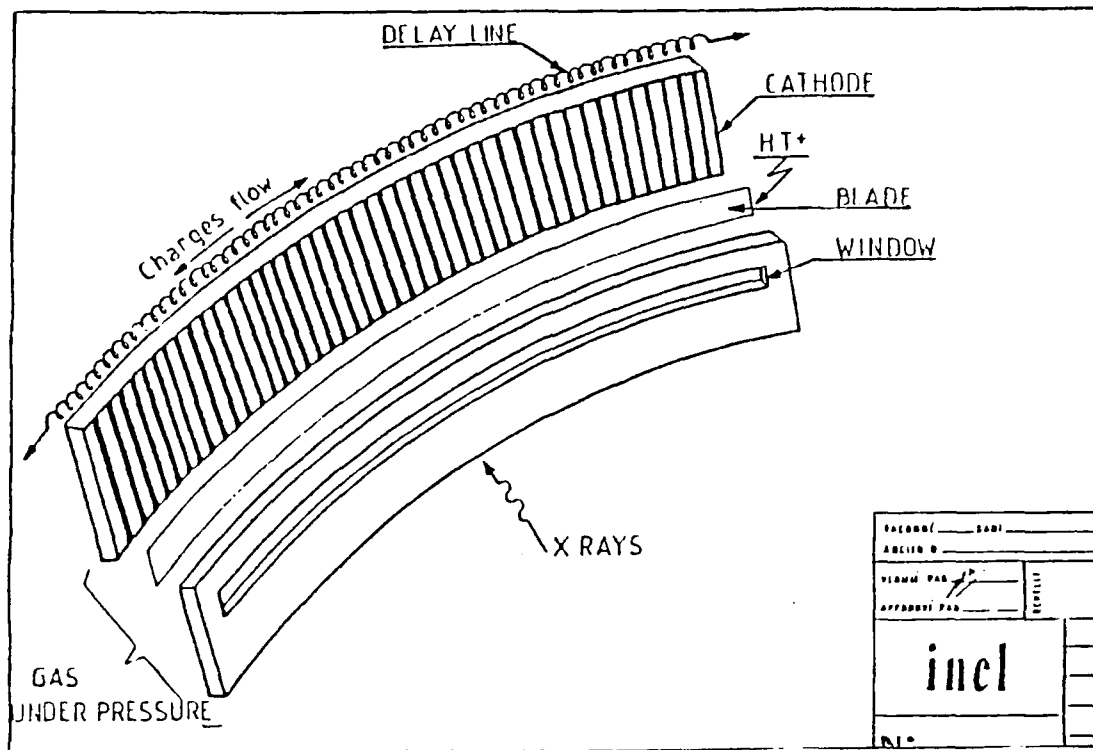


Figure 1 Schematic Illustrating the Construction of CPSD.

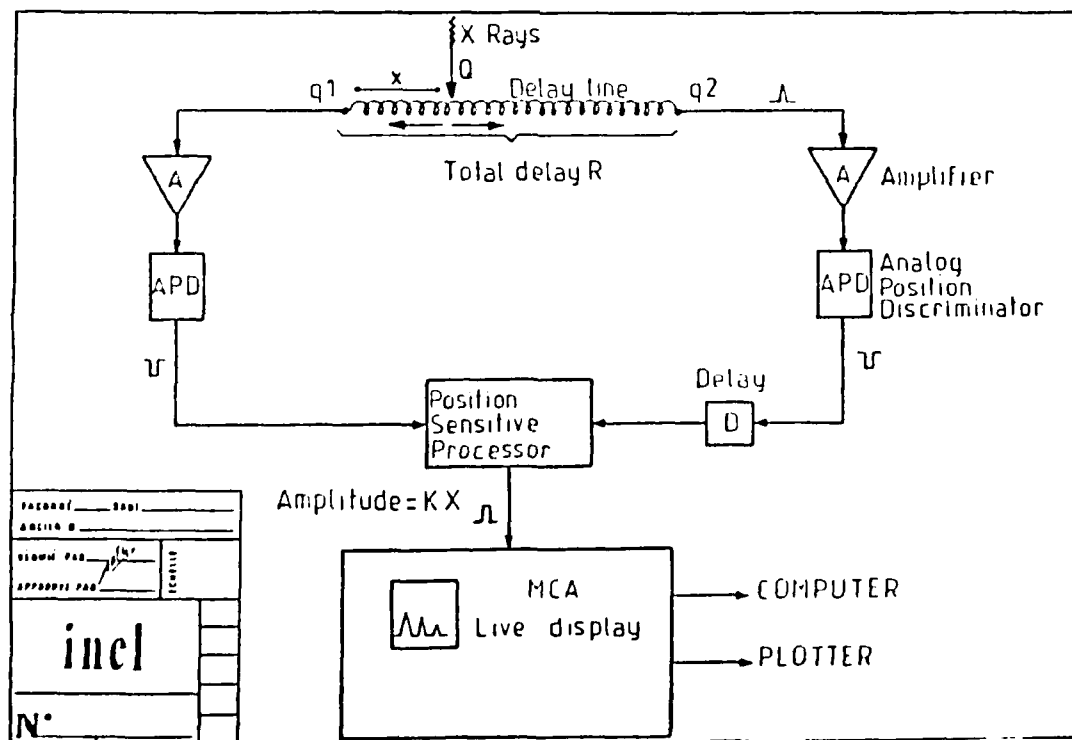


Figure 2 Electrical Circuit Illustrating the Operation of CPSD.

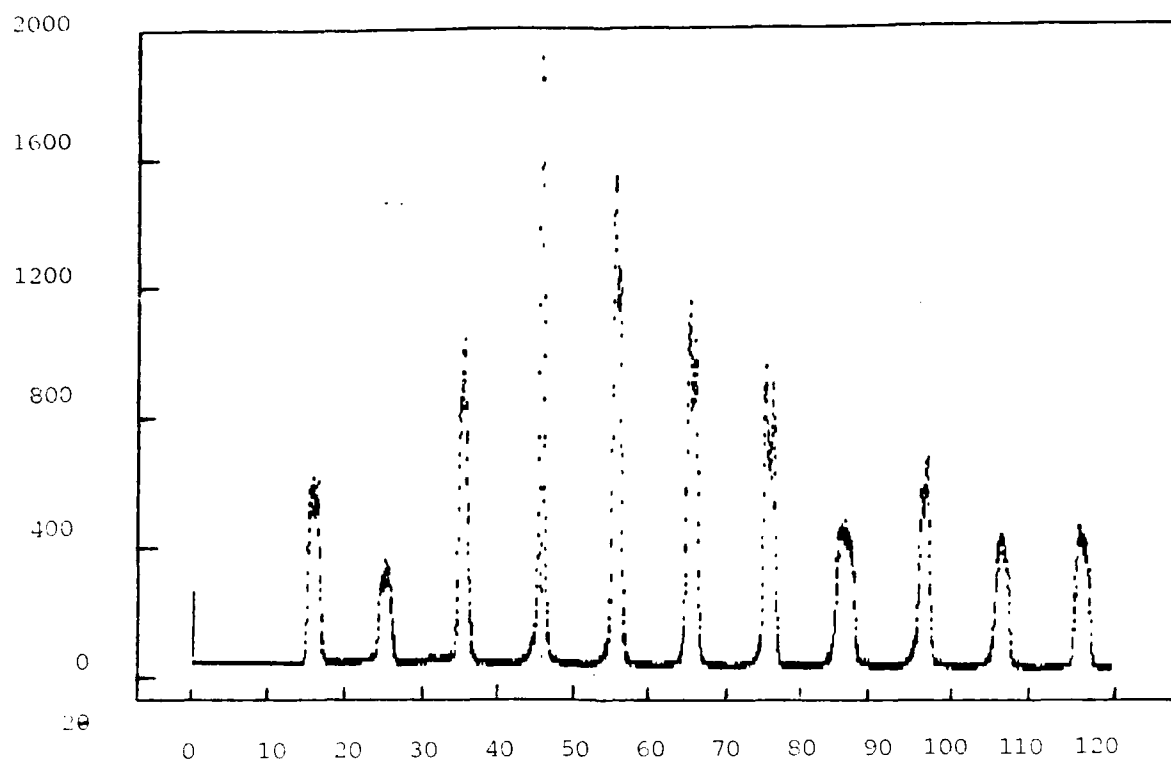


Figure 3 Calibration Run (using Main Beam).

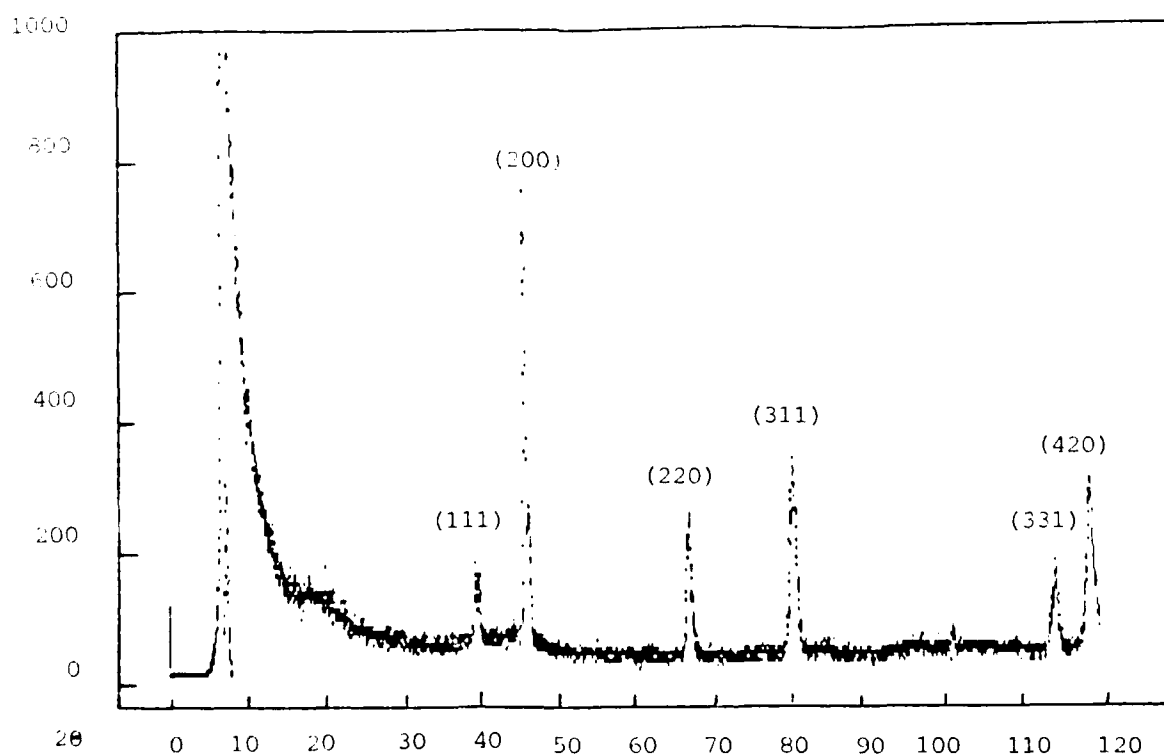


Figure 4 Aluminum Diffraction Pattern Obtained using CPSD.

TABLE I

2	Channel #	Number of Channels per 10° (Δ C/10°)
134	529	324
125	853	349
115	1202	340
105	1542	331
95	1873	336
85	2209	344
75	2553	343
65	2896	385
55	3281	325
45	3606	353
35	3959	346
25	4305	346
15	4316	

$C/10^{\circ}\text{C} = 343.3 = \text{Average Number of Channels per } 10^{\circ} \text{ Span}$

$C/1^{\circ}\text{C} = 34.3 = \text{Number of Channels per Degree}$

TABLE II

(hkl)	<sup>0</sup> (d) Å	2θ (in degrees)
(111)	2.3373	38.4690
(200)	2.0225	44.7556
(220)	1.4157	65.8958
(311)	1.2061	79.3462
(331)	0.9222	113.2058
(420)	0.8995	117.7380

Aluminum Powder Diffraction Data Obtained using CPD.